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Development of an Integrated in-situ Remediation Technology

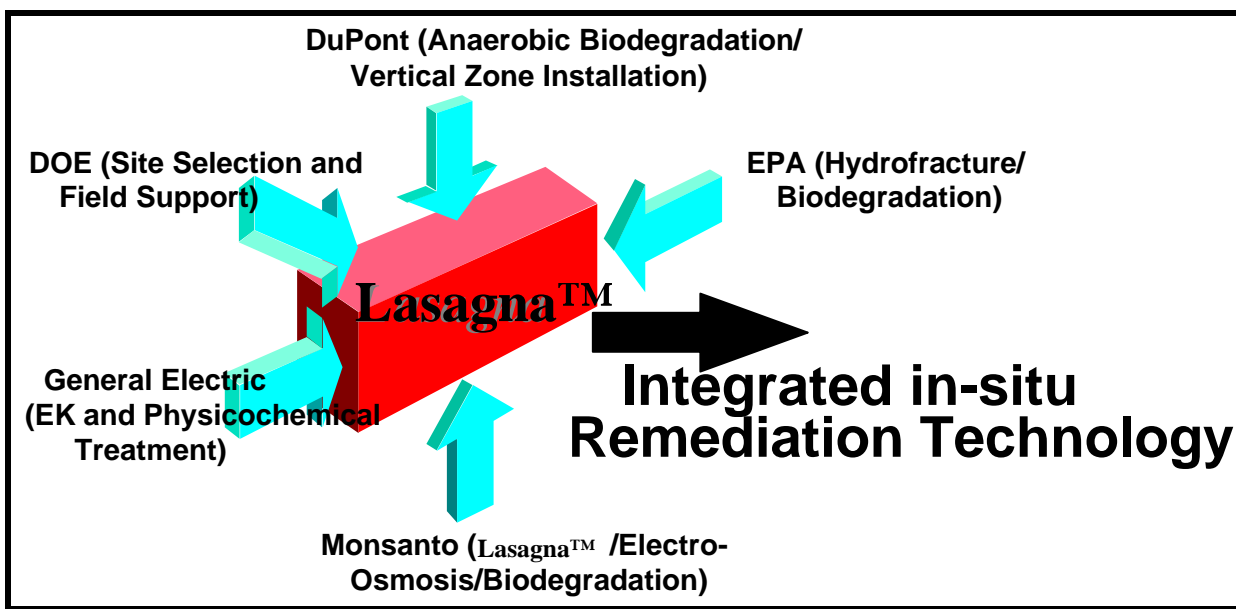
Draft Topical Report for Task #7.2 entitled, "Field Scale Studies" (January 10, 1996 - December 31, 1997)

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A. Executive Summary

Development of an Integrated in-situ Remediation Technology

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Draft Topical Report for Task # 7.2 - "Field Scale Test"

(January 10, 1996 - December 31, 1997)

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Abstract

Contamination in low-permeability soils poses a significant technical challenge to in-situ remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing in-situ treatments such as bioremediation, vapor extraction, and pump and treat rather ineffective when applied to low permeability soils present at many contaminated sites. The technology is an integrated in-situ treatment in which established geotechnical methods are used to install degradation zones directly in the contaminated soil and electro-osmosis is utilized to move the contaminants back and forth through those zones until the treatment is completed. The present Topical Report for Task #7.2 summarizes the Field Scale Test conducted by Monsanto Company, DuPont, and General Electric.

B. Acronyms and Abbreviations

DCE	Dichloroethylene
DNAPL	Dense Non-Aqueous Phase Liquid
DOE	Department of Energy
DuPont	E. I. du Pont de Nemours & Co., Inc.
EPA	Environmental Protection Agency
GC	gas chromatography
GE	General Electric Company
LMES	Lockheed Martin Energy Systems
ROD	Record of Decision
RREL	Risk Reduction Engineering Laboratory
SWMU	Solid Waste Management Unit
TCE	trichloroethylene
VC	vinyl chloride

C. Units

C, °C	Celsius, degrees Celsius
cm	centimeters
d, D	days
deg	degrees
F, °F	Fahrenheit, degrees Fahrenheit
f, ft	feet
g	grams
gal, GAL	gallons
h, hr	hours
in	inches
k, K	thousand
kg	kilograms
l, L	liters
lb, lbs	pound(s)
m	meter
mg	milligrams
min	minutes
ml, mL	milliliters
mm	millimeters
ppb	parts per billion
ppm, ppmw	parts per million (by weight)
psi	pounds per square inch
µg	micrograms
µl, µL	microliters
"	inches
'	feet
#	pounds

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Statement of the Problem

Contamination in low permeability soils poses a significant technical challenge to *in-situ* remediation efforts. Poor accessibility to the contaminants and difficulty in delivery of treatment reagents have rendered existing *in-situ* treatments such as bioremediation, vapor extraction, and pump and treat, rather ineffective when applied to low-permeability soils present at many contaminated sites.

The Solution

The proposed technology combines electro-osmosis with treatment zones that are installed directly in the contaminated soils to form an integrated *in-situ* remedial process. Electro-osmosis is an established civil engineering technique and is well known for its effectiveness, utilizing very low power consumption, in moving water uniformly through low-permeability soils.

Conceptually, the integrated technology could treat organic and inorganic contamination, as well as mixed wastes. Once developed, the technology will have tremendous benefits over existing ones in many aspects including environmental impacts, cost effectiveness, waste generation, treatment flexibility, and breadth of applications.

Consortium Description

A Consortium has been formed consisting of Monsanto, E. I. du Pont de Nemours & Co., Inc. (DuPont), and General Electric (GE), with participation from the Environmental Protection Agency (EPA) Office of Research and Development, and the Department of Energy (DOE) Environmental Management Office of Science and Technology. The five members of this group are leaders in their represented technologies and hold significant patents and intellectual property which, in concert, may form an integrated solution for soil treatment. The figure on the cover page shows a schematic diagram of the various technologies and support services which the government/industry consortium has integrated for the development of an *in-situ* remediation technology.

Project History

To date, this project has been conducted in two parts: Phase I and Phase IIa. A Management Plan was originally prepared for Phase I of this project by Monsanto and submitted on November 30, 1994. That plan summarized the work plan which was developed in conjunction with DuPont, GE, EPA's Risk Reduction Engineering Laboratory (RREL), Lockheed Martin Energy Systems (LMES), and the Department of Energy. The DOE Gaseous Diffusion Plant in Paducah, Kentucky, was chosen as the site for the initial field tests. The specific contamination site selected at the Plant was Solid Waste Management Unit (SWMU) 91. For Phase I, the treatment cell selected to demonstrate the process measured 10 feet by 15 feet by 15 feet deep.

CDM Federal Programs Corporation was chosen to provide the on-site support of the field tests which were launched at the DOE site in November 1994. The Phase I experiment tested the combination of electro-osmosis and *in-situ* sorption in the treatment zones. Technology development was carried out under the present contract in Phases I and IIa by Monsanto, DuPont, and GE. These studies evaluated various degradation processes and their integration into the overall treatment scheme at bench and pilot scales.

Phase IIa was approved on January 18, 1996. For this phase, a significantly larger cell was selected, measuring 21 feet by 30 feet by 45 feet deep, and significant design changes were also implemented in the materials used to construct the electrodes and treatment zones. While Phase I was conducted to demonstrate the movement of TCE from the soil into the treatment zones, Phase IIa was conducted to demonstrate that Phase IIb (the full-scale remediation of the SWMU 91 site) would be successful. This latter phase included the use of zero-valent iron metal which degrades TCE to light hydrocarbons and chloride ions. In August of 1997, DOE advised that, based upon the performance of the *Lasagna*TM process during Phases I and IIa, *Lasagna*TM would be the preferred remedy given in the proposed Record of Decision (ROD). If signed, this ROD to be implemented in Phase IIb will be the first example of the use of *Lasagna*TM for the full-scale remediation of a TCE-contaminated clay site. ROD approval is expected in calendar-year 1998.

Technical Deliverables

Table E-1 summarizes the four topical reports which have been written to describe the results obtained from the Phase IIa research. This table also shows which organization is primarily responsible for the tasks and for preparing the topical reports. The present topical report summarizes Task #7.2.

Table E-1. List of Topical Reports and Responsible Company

Topical Report	Company
Task #3.1 - Emplacement Technology	DuPont
Tasks #3.2 - Modeling and Iron Dechlorination Studies	GE
Task #3.3 - <i>Lasagna</i> TM and Iron Dechlorination	Monsanto
Task #7.2 - Field Scale Test	Monsanto/DuPont/GE

Introduction

The *Lasagna*TM approach involves the synergistic combination of electrokinetics (EK) with treatment technologies. EK includes electro-osmosis (EO, transport of water) and electromigration (EM, transport of ions) induced by an applied dc electric field. EO has been used since the 1930s for dewatering clays, silts, and fine sands¹. Electrokinetics has recently received increasing attention as an *in-situ* method for remediating contaminated soils^{2, 3, 4, 5, 6, 7}. Contaminants in the soil are transported by EK to one of the electrodes for collection and further disposal. The mode of transport for organic contaminants is primarily through the EO flow from anode to cathode, whereas for metals and radionuclides the main mechanism for transport is ion migration under the electric field (EM). Depending upon their charge, ions can move to either electrode. Common heavy metals like lead and chromium are cationic (positively charged) when dissolved in water and move toward the cathode.

Advantages of electro-osmosis include (1) uniform water flow through heterogeneous soil, (2) a high degree of control of the flow direction, and (3) very low power consumption. As currently practiced, however, the technology is characterized by several limitations associated with electro-osmosis when applied to large-scale remedial applications. These include (1) long-term treatment duration (liquid flow rate induced by electro-osmosis is typically about 1 inch per day in clay soils), (2) the requirement for additional above-ground treatment, (3) unstable long-term operation resulting from soil drying and cracking, (4) inducement of a steep pH gradient in the soil bed, and (5) precipitation of metals and

¹ L. Casagrande, *BSCE*, 39:51-83 (1952).

² A. P. Shapiro, P. Renaud, and R. Probstein, "Preliminary Studies on the Removal of Chemical Species from Saturated Porous Media by Electroosmosis." In *Physicochemical Hydrodynamics*, Vol. 11, No. 5/6, pp. 785-802 (1989).

³ J. Hamed, Y. B. Acar, and R. J. Gale, *ASCE*, Vol. 112, pp. 241-271, February (1991).

⁴ C. J. Bruell and B. A. Segall, *J. Environ. Eng.*, Vol. 118, No. 1, pp 68-83, Jan/Feb 1992.

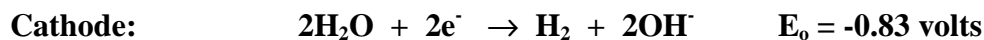
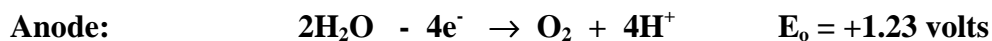
⁵ B. A. Segall, and C. J Bruell, *Environ. Eng.*, Vol. 118, No. 1, pp 84-100, Jan/Feb 1992.

⁶ Y. B. Acar, H. Li, and R. J. Gale, *ASCE*, Vol. 118, No. 11, pp. 1837-1852, November 1992.

⁷ A. P. Shapiro and R. F. Probstein, *Environ. Sci. Technol.* 27, pp. 283-291, 1993.

minerals near the cathode⁴⁻⁷. Recent efforts to mitigate the pH problem primarily involve conditioning the anode and cathode solutions through external water recirculating loops^{8, 9}.

The pH changes primarily result from water electrolysis as the predominant electrode reactions, generating acid at the anode and base at the cathode according to the following reactions:



where E_0 is the standard electrochemical potential.

The integrated *in-situ* treatment technology utilizes established geotechnical methods to emplace planar degradation or “treatment” zones directly in the contaminated soil, and electro-osmosis is utilized to transport the contaminants in water back and forth through these zones until the treatment is completed. Conceptually, the integrated technology could treat organic and inorganic contamination as well as mixed wastes. The process is termed “Lasagna” due to the many “layers” created by emplacement of the two electrodes and multiple treatment zones^{10, 11}.

The Phase I test (see Section E., Background, for project history) was a notable success, demonstrating, for the first time, scale-up of electrokinetics in conjunction with very high removal of TCE (~99%) from the contaminated soil. The Phase I experiment also demonstrated, for the first time, a strong possibility that Dense Non-Aqueous Phase Liquid (DNAPL) could be moved by the LasagnaTM process. The results were summarized in a report entitled “Development of an Integrated *in-situ* Remediation Technology, Tasks #12 and 13” prepared by Monsanto for the DOE under contract number DE-AR21-94MC31185¹².

⁸ R. Lageman “Electroreclamation - Applications in The Netherlands.” *Environ. Sci. Technol.*, pp 2648-50, Vol. 27, No. 13, 1993.

⁹ Y. B. Acar and A. N. Alshawabkeh, “Principle of Electrokinetic Remediation” *Environ. Sci. Technol.*, pp 2638-47, Vol. 27, No. 13, 1993.

¹⁰ Sa V. Ho, P. Wayne Sheridan, Christopher J. Athmer, Michael A. Heitkamp, Joan M. Brackin, Deborah Weber, and Philip H. Brodsky, “Integrated in situ Soil Remediation Technology - The LasagnaTM Process.” *Environ. Sci. Tech.*, vol 29., No. 10, 2528-2534 (1995).

¹¹ P. H. Brodsky and S. V. Ho, “In-Situ Remediation of Contaminated Soils,” U.S. Patent 5,398,756, issued March 21, 1995.

¹² C. J. Athmer, S. V. Ho, B. M. Hughes, P. W. Sheridan, P. H. Brodsky, A. P. Shapiro, R. F. Thornton, J. J. Salvo, D. S. Schultz, R. C. Landis, R. Griffith, and S. H. Shoemaker, “Development of an Integrated *in-situ* Remediation Technology,” Topical Report for Tasks 12 and 13, Report for DOE contract number DE-AR21-94MC31185, 1996.

The second phase, Phase IIa, (again, see Section E., Project History) represented a major step forward in terms of treating TCE *in situ* as well as extending the treatment to whatever depth necessary to clean up the Paducah site. Based on extensive data in the literature^{13, 14, 15, 16, 17, 18, 19, 20} and the consortium's studies, zero-valent iron in the form of iron filings was chosen as the reagent to degrade TCE. Issues related to TCE degradation in the *Lasagna*TM configuration included:

- effectiveness of iron filings in an electro-osmotic environment
- degradation by-products of TCE
- effectiveness of iron for degrading DNAPL TCE
- role of electrodes in TCE degradation

After sufficient laboratory and pilot testing, Phase IIa was begun to demonstrate the effectiveness of the technology for full-scale cleanup. For this phase, the two electrodes were 30 feet by 45 feet (deep) and were spaced 21 feet apart. Important issues addressed in this demonstration included:

¹³ T. Senzaki and Y. Kumagai, 1989. "Removal of Chlorinated Organic Compounds from Wastewater by Reduction Process: II. Treatment of Trichloroethylene with Powder. *Kogyo Yosui*. 369, 19-25.

¹⁴ R. W. Gillham, and S. F. O'Hannesin, 1994. *Ground Water* 32, 958-967.

¹⁵ R. W. Puls, R. M. Powell, and C. J. Paul, (1995). "In Situ Remediation of Ground Water Contaminated with Chromate and Chlorinated Solvents Using Zero Valent Iron: A Field Study," Natl. Meet. Amer. Chem. Soc., Div. Environs. Chem. 35, 788-791.

¹⁶ D. R. Burris, T. J. Campbell, and V. S. Manoranjan, (1995). "Sorption of Trichloroethylene and Tetrachloroethylene in a Batch Reactive Iron Water System." *Environ. Sci. Technol.* 29(11): 2850-2855.

¹⁷ A. L. Roberts, A. Totten, W. A. Arnold, D. R. Burris, and T.J. Campbell, (1996). "Reductive Elimination of Chlorinated Ethylenes by Zero Valent Metals." *Environ. Sci. Technol.* 30(8), 2654-2659.

¹⁸ T. L. Johnson, M. M. Scherer, and P. G. Tratnyek, (1996). "Kinetics of Halogenated Organic Compound Degradation by Iron Metal." *Environ. Sci. Technol.* 30(8): 2634-2640.

¹⁹ W. S. Orth and R. W. Gillham, (1996). "Dechlorination of Trichloroethene in Aqueous Solution Using Fe⁰." *Environ. Sci. Technol.*, 30:60-71.

²⁰ T. J. Campbell, D. R. Burris, A. L. Roberts, and J. R. Wells, (1997). "Trichloroethylene and Tetrachloroethylene Reduction in Metallic Iron-Water-Vapor Batch System." *Environ. Toxicol. Chem.* 16(4), 625-630.

- design and installation of electrodes and treatment zones to a depth of 45 feet
- electrical effects of voltage, current, power, soil conductivity, heating, etc.
- long-term operation of the process
- extent of soil cleanup as a function of treatment time
- cost of treatment

The treatment cost of the *Lasagna*TM technology, which has been targeted at \$50-100/yd³, is a very key issue in this demonstration. In addition, field data were also utilized to calibrate a mathematical model of the process developed in Phase I. Once the technology is successfully demonstrated and meets cost target, *Lasagna*TM could be scaled up to clean up the entire contaminated site at the Paducah Gaseous Diffusion Plant (PGDP) cylinder drop test area. This report summarizes the *Lasagna*TM Phase IIa field test.

Materials and Methods

Analytical Procedures for Soil and Carbon

Soil sampling was conducted by Oak Ridge National Laboratory (ORNL) under the direction of Lockheed Martin Energy Systems (LMES, then Martin Marietta Energy Systems). TCE was extracted from the soil with hexane. Soil analysis was performed at the site using a gas chromatograph equipped with an electron capture detector (GC-EC). Carbon sampling was performed by ORNL and ESC. Carbon analysis was also performed by ORNL. Details of the sampling and analytical protocols and methods are documented in the Phase I Report¹² or the Quality Assurance Project Plan for this test²¹.

Installation & Operation

Emplacement Method

The field test covered a soil section 21 feet long by 30 feet wide and approximately 45 feet deep. The installation was performed by Nilex Corporation of Englewood, Colorado under the direction of the consortium members DuPont and Monsanto. A specially designed mandrel/tremie tube system was used for introducing electrode and treatment zone materials. The mandrel was 20 inches wide by 2 inches thick (hollow) and approximately 55 feet long; it consisted of 4 tremie tubes measuring 2 inches by 5 inches welded together. The length of the mandrel allowed it to be driven 45 feet into the ground, at which point approximately 10 feet remained above ground. A crane and a vibratory hammer were used to move and drive the mandrel, which was mounted on a 60-foot mast tower. Materials

²¹ "Final Quality Assurance Project Plan (QAPP) for the Rapid Commercialization of an Integrated *in-situ* Remediation Technology," submitted to USDOE by Monsanto, March 3, 1997.

needed for each insertion were contained in a hopper fastened to the top end of the mandrel. The inserted materials were mixed in a cement mixer and were delivered to the mandrel system using a fork truck and cement bucket. All the materials were delivered to the site in bulk shipping bags that were filled with a convenient amount of material for mixing.

Once the grid was laid out for the installation of electrodes and treatment zones, the mandrel was positioned using the crane. The drives were overlapped by 5 inches (1 whole tremie) to assure longitudinal continuity of the electrode or treatment zone materials. Each zone was formed by sequentially making 24 drives, side by side 45 feet deep, along the 30-foot length of the unit, thereby creating a planar "curtain" of either electrode or treatment zone material (as applicable).

A conceptual drawing of the experiment installation at the Paducah plant is presented in Figure F-1.

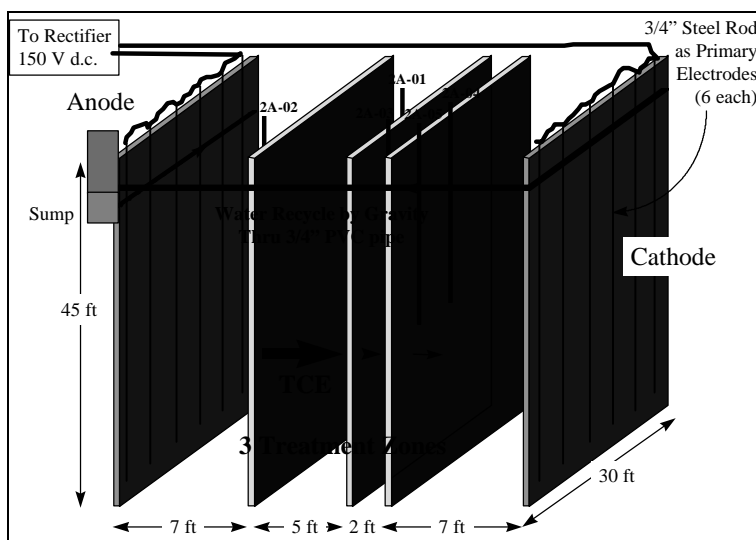


Figure F-1. Conceptual Drawing of the Phase IIa Installation

Dimensions and Composition of Electrodes and Treatment Zones

The two 30- by 45-foot electrode zones consisted of 1 1/2-inch thick curtains of material, and the two zones were spaced 21 feet apart. The electrode material consisted of a dry mixture of 50/50 by volume Peerless iron filings and Loresco coke. This particular type of coke is commercially available and was specially designed as a backfill material for cathodic protection of buried metal systems such as pipes and tanks. The use of iron filings dictated that iron corrosion would be the predominant reaction at the anode instead of water electrolysis, thus minimizing acid (H^+) formation, which would reduce the effectiveness of electro-osmosis. Six steel rods (3/4" diameter, hot rolled) were inserted into the electrode materials of each electrode, approximately 5 feet apart, to a depth of 40 feet to effect uniform current distribution. The rods were connected in parallel to the main power cable, which was laid along the ground using cathodic-protection welding techniques. Current levels could be measured in each rod by measuring the difference in current flow in the main

cable before and after each steel rod. The steel rods served as the primary conductors and distributed the current throughout the anode and cathode materials. Tests performed after installation using a car battery connected to the outermost rods demonstrated an apparent electrode conductivity of 4.5 S/m. This was approximately 200 times higher than the soil conductivity.

Three treatment zones, each also 1 1/2 inches thick, were emplaced between the electrodes. The first treatment zone was emplaced 7 feet from the anode, the second 5 feet from the first, and the third 2 feet from the second. Treatment zone material consisted of Peerless iron filings (60% wt) suspended in wet kaolin clay, which formed a slurry that was poured down into the hollow mandrel to the 45-foot depth. The original design called for iron content of 8 vol% in clay, but excess water was needed in the clay slurry to make the viscosity high enough to allow it to pour down into the mandrel effectively. Unfortunately, when the mandrel was withdrawn, the resultant high viscosity allowed the slurry to spew up and out of the treatment zone “slot”; therefore, it was necessary to increase the consistency of the slurry to prevent loss of the minimum intended composition. Consequently, the actual volume of iron filings in the slurry was increased to 26 vol% (or 1.61 g Fe/cm³), which was more than 3 times the design level. Also, the clay slurry contained 50 wt% water, much higher than the saturation level of about 40% for kaolin clay. It was therefore anticipated that the overall material “bulk” in the treatment zones would shrink downward during the operation as a result of lateral water migration (due to electro-osmotic flow); however, since the 5 feet of gravel on the ground surface was not contaminated, no treatment zone was needed for this section, thus permitting the treatment material to shrink downward as much as 5 feet (i.e., to the top stratum of contaminated soil) without serious detriment. All materials chosen for electrodes and treatment zones are innocuous to the environment and are designed to remain in-place after the cleanup is completed. This is an important consideration in implementing the *Lasagna*TM technology to minimize both treatment costs and detrimental impact upon the environment.

Monitoring Probes

The voltage, temperature, water, and carbon monitoring systems were installed with the Nilex equipment using a 4-inch by 4-inch square tube tremie 50 feet long. The tremie was driven in the ground to the appropriate depth, the monitoring equipment was installed, and then the tremie was removed leaving the monitor in place. This was a no-waste and extremely fast method of installing piezometer and monitoring equipment. The carbon sock wells contained a 25-foot long sock filled with granular activated carbon. Initially, a plastic tie-wrap was fastened around the sock at 1-foot intervals to allow for discrete measurement of the TCE concentrations with depth; however, in addition, for the second generation socks, several short segments of the socks were filled with bentonite clay to much more effectively seal off any vertical TCE migration by hydraulic or gaseous diffusion, thus significantly improving the integrity of TCE measurements by depth. The bentonite seals were placed at about 12 and 18 feet deep. Figure F-2 shows the location of the installed monitoring equipment and piezometers.

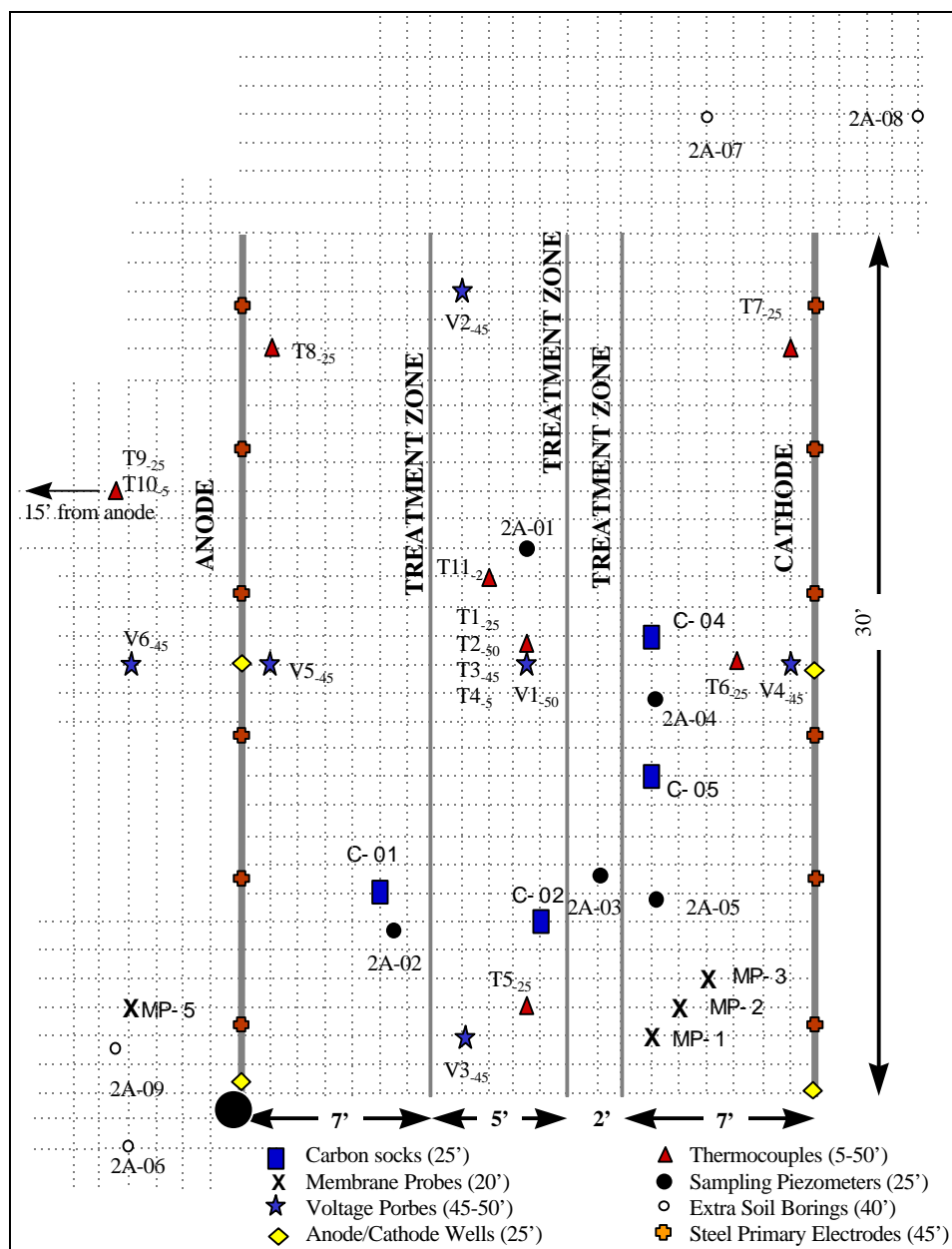


Figure F-2. Location of Monitoring Points

Twelve thermocouples and six multi-depth voltage probes were installed in the unit. The thermocouples were installed at various depths and locations to monitor the temperature rise in the soil generated as a result of resistive heating. Each voltage probe allowed measurements of the voltage potential at vertical increments of 5 feet. A solar-powered data station, constructed by the Monsanto electronic shop, consisted of a digital thermometer and a multiposition switch for temperature measurements and a digital voltmeter with two multiposition switches for the voltage measurements. For voltage measurements, one switch allowed selection of a specific voltage probe and the other the desired depth.

Water Management System

The fluid circulation is presented in Figure F-1. Overflow “wells” installed in two of the cathode drives allowed the water which migrates to or “mounds” at the cathode to be transferred by horizontal pipes to a sump for reuse at the anode. Wells were also installed at the anode in two drives which were connected to the sump. This allowed the water from the sump to flow into these two wells and keep the anode moist.

To help keep the water handling systems from freezing, the horizontal pipes as well as the sump were installed below grade. The cathode side of the system was installed 4 ½ feet below grade and the anode piping 5 feet below grade to provide a downward gradient toward the anode. The 6-inch drop in water levels allowed measurement of the fluid flow rate as the water drained out of the cathode piping into the sump; this setup also prevented electrical shorting between anode and cathode through the water conduit. This direct recycling of water, cations, and high pH collected at the cathode back to the anode is one of the advantageous features of the *Lasagna*TM process.

Electrical System

Power to the test site was supplied with a diesel-run Olympian Power Generator CT-110 rated at 100 kw. A Rapid Power Technology model SCRA 410 C425 rectifier provided the DC power to the field unit. About 50 feet of heavy copper wire cable (0000 size) was used to connect the power rectifier to each electrode.

Soil Sampling

Five soil sampling locations were chosen based on the initial experimental design. These locations corresponded to the 5 piezometers installed (previously mentioned). Locations 2A-04 and 2A-05 were about 1 foot behind the last treatment zone (nearest the cathode). Location 2A-03 was between the 2-footspaced treatment zones. This location was designed to demonstrate the effect of closely spaced treatment zones in limiting “reverse” migration. The locations 2A-02 and 2A-01 provided for “upgradient” samples which should demonstrate limited changes during the first 6 months of operation. All soil sampling was conducted by ORNL. Soil samples were collected by taking 4-foot-long soil cores from the sampling hole. Each core was then sub-cored to attain soil samples at 1-foot intervals. TCE was extracted using hexane and analyzed on-site in a nearby laboratory trailer. More information on the soil sampling data and methods can be found in a related report.

Electro-osmotic Permeability Calculation: The electro-osmotic permeability can be calculated using the following equation:

$$Q = k_e \Delta E A$$

where Q = electro-osmosis volumetric flowrate (cm³/sec)

k_e = coefficient of electro-osmotic permeability (cm²/volt-sec)

ΔE = voltage gradient applied across the treatment cell (volt/cm)

A = cross-sectional area perpendicular to the direction of flow (cm²)

The electro-osmotic flow rate is thus proportional to the applied voltage gradient, and the electro-osmotic permeability has the units of velocity over field strength (cm/sec over volt/cm). The cross sectional area was 1.115×10^6 cm² for the Phase IIa test. Flow rate measurements were performed using a beaker and a stop watch. The flow of water from the cathode pipe into the sump was considered to be all cathode water. This assumption was considered valid since, when the power was shut off, the flow rate slowed down significantly and then stopped entirely. The flow rate measurements were normally not performed until several days after any significant rainfall.

Results and Discussion

Site & Soil Characteristics

The area at the Paducah Gaseous Diffusion Plant cylinder drop-test site is mostly clay with gravel and clay overburden and has been used as a truck road. The contaminant at this site is primarily trichloroethylene (TCE), the concentration of which ranges from below 1 mg/kg (ppm) to approximately 1,500 mg/kg. The vertical and lateral extent of the TCE plume at this site could be estimated from a number of soil and water samples taken over the years. With a soil density of 2 g/cc, 40% porosity and 20% moisture content, a soil concentration of 225 mg TCE/kg would result in pore water saturated with TCE (1100 mg/kg). Thus, a level of 1,500 ppm is definitely an indication of the presence of DNAPL in the area. Table F-1 lists the characteristics of the Paducah soil and Figure F-3 shows the calculated contour map of the highest TCE concentrations found in the soil.

Table F-1. Paducah Soil Characteristics

Soil Type:	Clay Loam
Sand Content:	22 Percent
Silt Content:	46 Percent
Clay Content:	32 Percent
Moisture Content:	15-18 Percent
Organic Carbon Content:	0.2 Percent
Cation Exchange Capacity:	13.4 meq/100 g
Porosity:	0.4
Bulk Density:	2.0 g/cc
Electroosmotic Conductivity	1.2×10^{-5} cm ² /v-sec
Hydraulic Conductivity (estimated)	1×10^{-7} cm/sec

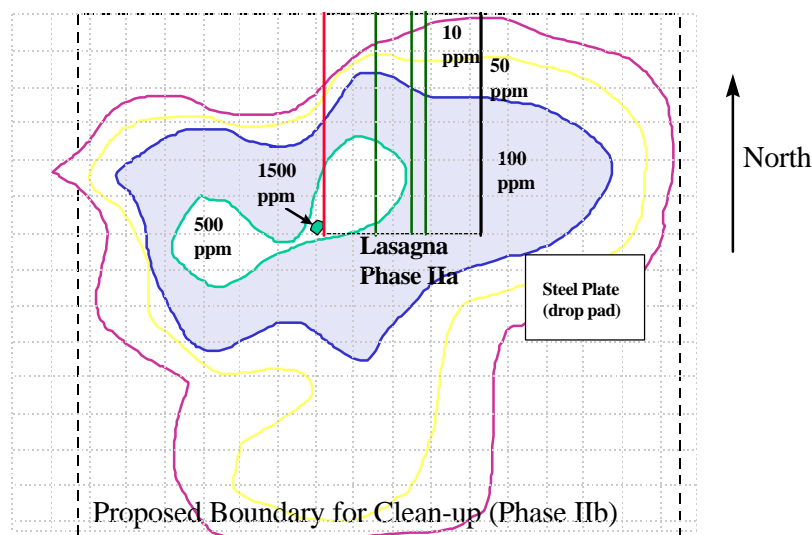


Figure F-3. Highest TCE Concentrations Detected in Zones Shown (1- to 40-Foot Depth)

In preparation for the Phase IIa field test, nine soil borings were made to confirm the northern edge of the plume and to determine the baseline of TCE concentration in the test area. Soil samples were taken at 1-foot intervals to a depth of 40 feet. The TCE contamination appeared to taper off to below detection limits at about 30 to 35 feet deep. It was determined from the data to install the *Lasagna*TM system to a depth of 45 feet to ensure complete cleanup. The regional aquifer is approximately 60 feet below grade in this area.

Electrokinetic Effects

The field installation was accomplished during June, July, and August 1996. The experiment was started (power on) on August 18, 1996 and the power-on period lasted almost 1 year, until early August 1997. The system was shut down for 3 weeks in March, 1997 for soil sampling.

Initially, the voltage was set at 150 volts and 110 amps DC. The rectifier was originally configured to operate at 480 volts AC input; however, this configuration caused a large mismatch in the voltages, resulting in a large AC component (30%). This was undesirable because, while AC power contributes to heating up the soil, it does not induce electro-osmosis; therefore, any AC component results in lower efficiency. Consequently, the generator was changed on October 1, 1996 and the rectifier was modified to operate at 240 volts AC. This lowered the AC component to less than 5% of the total power. The voltage was then set to 200 volts and 200 amps DC. As the temperature rises, the electrical conductivity of the soil also increases; therefore, it is necessary to adjust for this at some point to prevent ultimate overheating; consequently, when the temperature reached approximately 80°C, the power was reduced to 120 volts and 120 amps DC and then adjusted to 150 to 180 volts. After 160 days of operation, the core temperature at the center of the treatment cell reached a maximum of 83°C. The average soil temperature (as compared to core temperature) increased from 18°C to a peak of 60°C between 5 and 6

months after power on, and then stabilized to approximately 50°C until the end of the test.

Temperature, voltage profiles, groundwater quality, and water flow rates were monitored for the duration of the experiment. The distance the water front traveled during the experiment was approximately 5.5 feet, resulting in 2 ½ pore volumes through the 2-foot-interval treatment zone. Figure F-4 shows the voltage and current data for the experiment as well as the pore water travel distance. The negative numbers signify reverse polarity. Figures 5 and 6 show the temperature trends at the 25-foot depth across the site and the temperature trends of the probes at the center of the unit. Temperature is very important in several respects. First, elevated temperatures increase the reaction rate of the degradation with iron filings. Second, and most importantly, the diffusion and dissolution rate of TCE in water increase with increasing temperature. It also happens that the viscosity of water decreases as the temperature increases. This enhancement is almost perfectly offset by the electrical conductivity increase due to increasing temperature; however, the prescribed adjustment - decreasing the applied voltage - has the undesirable effect of reducing the electro-osmotic driving force, thereby reducing the flow rate.

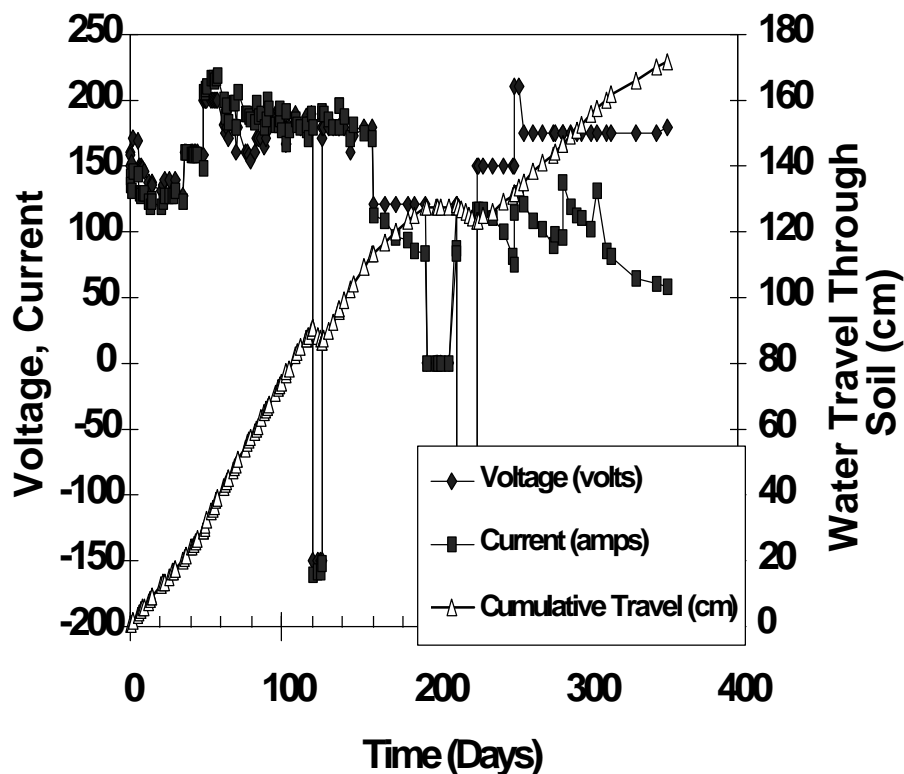


Figure F-4. Overall Voltage, Current, and Pore Water Travel Data

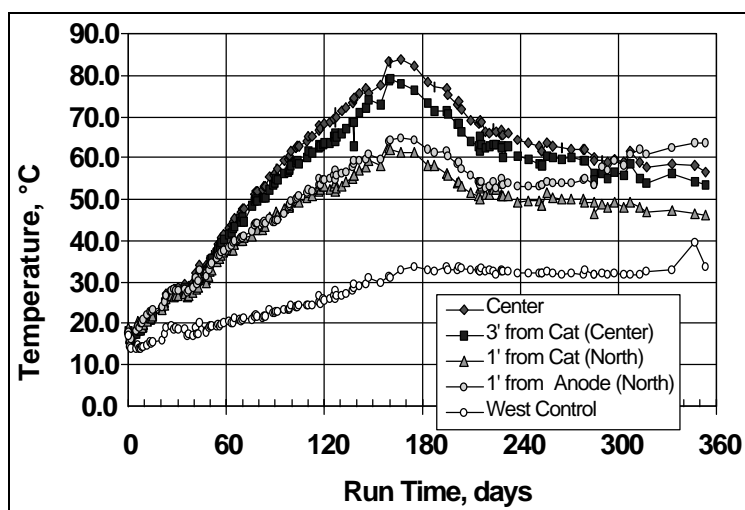


Figure F-5. Temperature Trends at 25 ft Depth

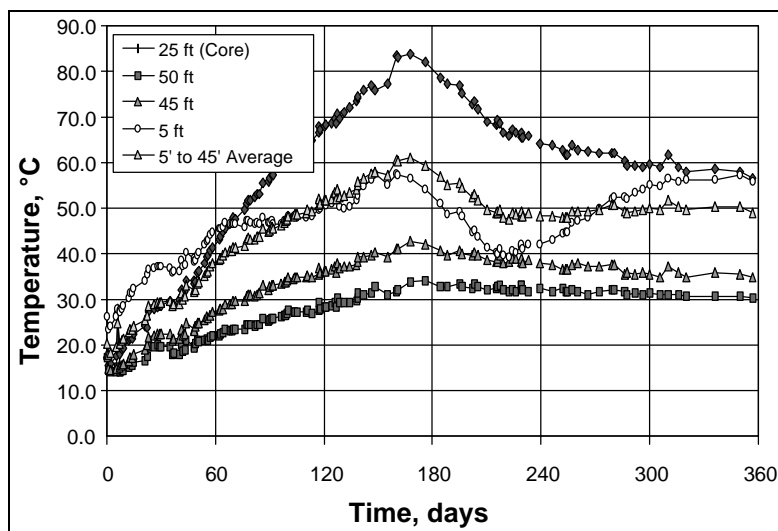


Figure F-6. Temperature Profile at Center of Test Site

Water flow-rates measured throughout the test period correlated well with the predicted flow rates based on the electro-osmotic permeability determined in the laboratory and the Phase I field test. The k_e calculated for the laboratory experiments and the Phase I field test was $1.2 \times 10^{-5} \text{ cm}^2/\text{volt-sec}$. Figure F-7 shows the measured and predicted flow rates, and the cumulative pore volumes of water passed through the system by electro-osmosis. Appendix A contains the spreadsheets of the recorded field data including temperatures, voltage, current, and flow rate. The water in the anode and cathode was monitored on a regular basis for TCE and chloride content and for pH and specific conductance. The cathode water (and the sump) quickly became alkaline, as expected. The pH at the cathode rose quickly to over 12 and the conductivity rose to over 15,000 $\mu\text{S}/\text{cm}$. The water quality at the anode was influenced strongly by the recirculating cathode fluid and therefore could not be accurately determined. The pH was about .5 to 2 pH units lower than at the cathode.

and the specific conductance was approximately 50 percent of cathode readings. In the laboratory and first field test, the pH at the anode remained approximately 6, while the specific conductance steadily increased. The dissolution of the iron at the anode and recycling of the cathode fluid was found to help stabilize the pH while the accumulation of anions, such as chloride and sulfate, caused the conductivity of the solution to raise steadily at the anode.

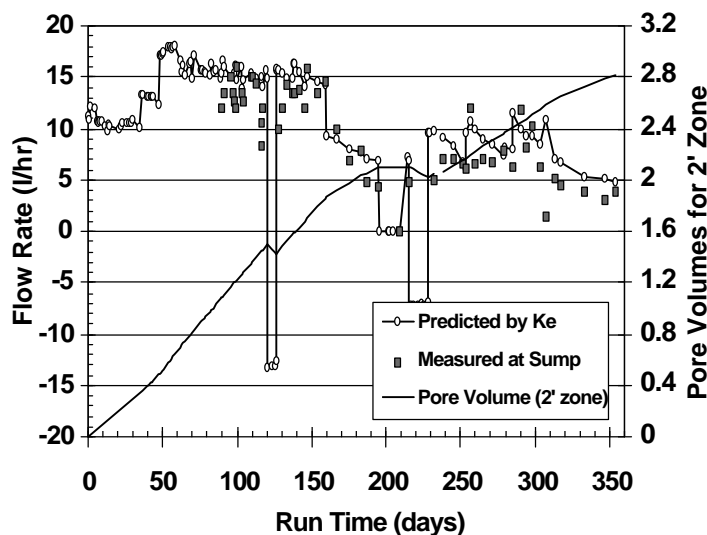


Figure F-7. Flow Rate Measured vs Predicted

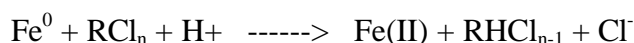
Initially, voltage distribution in the soil between the two electrodes was reasonably uniform. After approximately 5 months of operation, however, the voltage profile at the anode began to deteriorate. An investigation revealed that the water distribution wells at the anode were filled with clay, thus preventing the return water from “re-wetting” the anode and the nearby soil regions. It is possible that soil intruded into the electrode area, causing a significant reduction in its hydraulic permeability. Once the electrode begins to dehydrate, the resistance increases along with temperature, causing yet more dehydration. During the March 1997 soil sampling, three new anode wells were installed in an attempt to remedy this condition. The soil samples obtained exhibited spots of very dry, reddish, “crusty” material and a quantity of wet, black, loose material. The exact composition of this material and its formation process was not conclusively determined. In any case, the unit did operate more effectively after adding the three new wells, but not as effectively as at the original start up. That operation was impaired was evidenced by the fact that the temperature at the anode gradually rose above that of all other areas of the unit, including the center core.

Overall, the electro-osmotic conductivity, pH, and conductivity trends, power requirements, temperature trends, and operational stability all were in agreement with laboratory results. It is believed that the dehydration encountered at the anode was due primarily to an inefficient water distribution system, which failed to keep the anode

sufficiently moist, as designed, for optimum current distribution. This is a key lesson learned from the test, and a more effective water distribution system will be incorporated in the design for the full-scale cleanup.

TCE Removal

In Phase IIa, the basic chemical reactions between Fe and TCE were utilized for degrading TCE in a thin treatment zone containing iron filings and clay. The dechlorination of TCE using zero-valent iron has been studied extensively by many research groups¹³⁻²⁰. The effectiveness of this approach has been demonstrated either as permeable reactive walls or packed bed reactors at many field sites^{22, 23, 24}. It is believed that the dechlorination goes through a step-by-step process in which one chlorine atom is removed each time:



where R stands for hydrocarbon. According to this mechanism, TCE dechlorination by-products would occur in the following order: dichloroethylene (DCE), vinyl chloride (VC), ethylene, and ethane. However, while ethylene and ethane are readily observed as reaction by-products, very little of the intermediates DCE and VC is typically detected, probably because they remain bound to the iron surface and undergo further dechlorination.

Dechlorination Rates and Design Criteria For Treatment Zones

The rate of TCE dechlorination was measured by GE researchers using the Paducah groundwater both in batch (stirred pot) and continuous (packed bed) mode. The basic rate constant determined from these measurements is $k = 0.08 \text{ ccH}_2\text{O/hr-g Fe}$, which for a packing density of 2.41 g Fe/cm^3 and 0.614 packing porosity translates into a first order rate constant of 0.31 hr^{-1} , or a half life of 2.2 hr at room temperature. The GE study also investigated the dechlorination of TCE daughter products, such as dichloroethylene (DCE) and vinyl chloride (VC), which actually degrade more slowly than TCE: half life of 5.2 hr for c-DCE and of 3.3 hr for VC at 25°C . These data were utilized in the design of the

²² R. E. Gillham, 1995. "Resurgence of Research Concerning Organic Transformations Enhanced by Zero-Valent Metals and Potential Application in Remediation of Contaminated Ground Water." Natl. Meet Amer. Chem. Soc., Div. Environ. Chem. 35, 691-694.

²³ R. W. Puls, R. M. Powell, and C. J. Paul, (1995). "In situ Remediation of Ground Water Contaminated with Chromate and Chlorinated Solvents Using Zero Valent Iron: A Field Study." Natl. Meet Amer. Chem. Soc., Div. Environ. Chem. 35, 788-791.

²⁴ C. L. Yamane, J. D. Gallinatti, F. S. Szerdy, T. A. Delfino, D. A. Hankins, and J. L. Vogan, 1995. "Installation of a Subsurface Groundwater Treatment Wall Composed of Granular Zero-Valent Iron." Natl. Meet Amer. Chem. Soc., Div. Environ. Chem. 35, 792-795.

treatment zones to ensure complete destruction of TCE as well as these daughter products, especially VC.

Key considerations in the design of the treatment zones for Phase IIa were:

- ease of installation
- sufficient residence time for complete destruction of TCE and its daughter products, especially VC
- optimum level of iron, balancing between cost and the need for excess iron to ensure performance (rate and stability)
- minimization of TCE loss through volatilization in the treatment zones.

At the targeted voltage gradient of 0.25 volt/cm, the velocity of water moving through the Paducah clay soil is approximately 0.32 cm/day. Calculations based on the GE rate data showed that a treatment zone thickness of 2 inches containing 100% iron much more than required for complete destruction of TCE and its daughter products. It was therefore decided to mix iron filings with an inert material. Sand and clay were the two obvious options considered. Clay was chosen because it offers the following advantages: higher stability in an electro-osmotic environment (better water retention), minimum TCE loss from volatilization, ease of installation as a slurry, and it provides a better medium for keeping the iron particles dispersed throughout the 45-foot depth.

The following table shows the estimated half life values for TCE, c-DCE and VC at 25, 40 and 60°C for an 8 vol% iron packing (0.5 gFe/cm³).

Temperature, C°	Half Life in hr		
	TCE	c-DCE	VC
25	10.7	25.3	16.2
40	3.5	8.2	5.2
60	2.4	5.5	3.6

Based on the above half-life values, the amount of TCE, c-DCE, and VC converted as a result of passing through each treatment zone can be estimated as follows, assuming plug flow for the liquid:

Temperature, C°	% Conversion per Pass		
	TCE	c-DCE	VC
25	100	99.83	100
40	100	100	100
60	100	100	100

For pore water containing 1,000 ppm TCE, 10 ppm c-DCE, and VC each entering a treatment zone, the amounts of these chemicals in the pore water exiting the treatment zone are shown in the following table in ppm.

Temperature, C°	Effluent Concentration in ppm per pass		
	TCE	c-DCE	VC
25	0.0003	0.0168	0.0005
40	0	0	0
60	0	0	0

Thus, the actual amount of iron in the treatment zones (26 vol% or 1.61 g Fe/cm³) was more than sufficient to destroy TCE and its daughter products to very low levels, theoretically in a single pass. Note that dechlorination of TCE and its daughter products was occurring between 40 and 60°C during most of the operation. Additionally, the design

assumed at least 2 pore volumes, i.e. each fluid element would pass through treatment zones twice.

Dechlorination Results from Water Samples

Water from the monitoring piezometers 2A-01, 2A-02, 2A-03, 2A-04, 2A-05, and the cathode was sampled on a periodic basis throughout the experiment. As can be seen in Figure F-8, the TCE concentration in well 2A-03 dropped from the initial value of 150 ppm to 15 ppm at the end of the test. Wells 2A-04 and 2A-05, which were emplaced behind the last treatment zone, showed different trends. Although the initial readings at both sampling locations were approximately 500-600 ppm, the TCE levels in 2A-05 remained high longer, while readings at the 2A-04 location declined steadily to about 160 ppm. It is unclear why location 2A-04 cleaned up as expected while 2A-05 was much slower to clean up. Piezometer 2A-01 became dry after November 5, 1996 until April 1997, after which the TCE levels could again be recorded, and the level dropped to below 30 ppm. Piezometers 2A-01 and 2A-02 became dry in July and August, 1997 and could not be sampled.

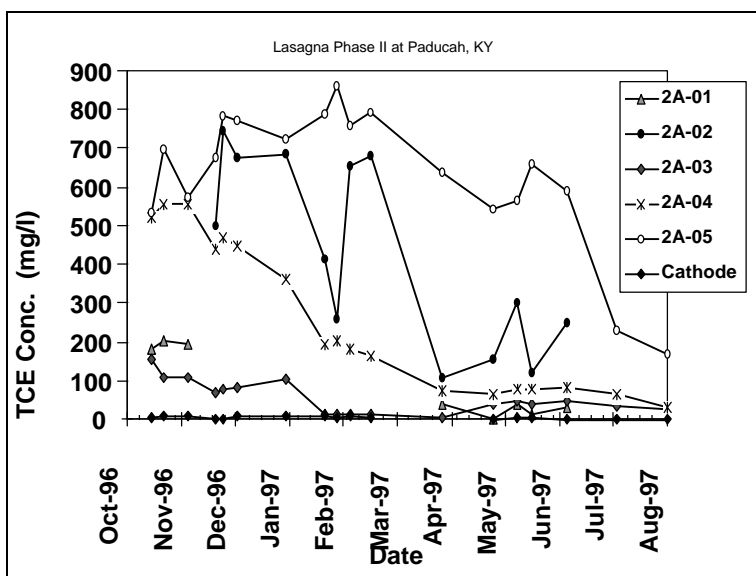


Figure F-8. Water TCE Concentration Trends

There is a strong possibility that some of the monitoring piezometers were contaminated with DNAPL. Some of the March water samples do not correlate well with the soil sampling. This is especially true for sample point 2A-05. The very high levels of TCE in the water (800 ppm) would surely indicate DNAPL in close proximity of the piezometer. The soil sampling, however, showed that TCE levels in the soil were well below DNAPL levels, even though a special effort was made to ensure DNAPL, if present, would be detected. To test the possibility of the piezometer 2A-05 contamination with DNAPL, in early June 1997, the well was purged several times, followed by sparging with helium for 72 hours. From that time on, the TCE levels in the pore water dropped steadily from approximately 700 to less than 200 ppm by early August, when the unit was shut down for final soil sampling.

Due to the strong evidence of DNAPL at various locations in the test plot, lab experiments were conducted to investigate the dechlorination of TCE. It was found that, as long as a minimal amount of water was present, the rate of TCE destruction for DNAPL would proceed at a rate comparable to that of TCE-saturated water. An unexpected outcome was the by-product distribution. For dissolved TCE, the products observed were primarily ethylene and ethane in equal amounts, with very little acetylene. When DNAPL was simulated, however, acetylene was determined to be the major dechlorination by-product, followed by ethylene, with very little ethane. This difference in by-product distribution provides an excellent indicator for determining TCE concentration levels in the field. The two reaction paths are shown in Appendix B as well as in the field results.

Water samples from various wells within the treatment cell and from a control well (MW 160) were taken six times during the test. The results are shown in Table F-2 and plotted in Figure F-9. It can be seen immediately that, throughout the test, samples from the control well showed high levels of TCE but non-detectable levels of the by-product gases ethylene, ethane, and acetylene. In contrast, all the samples from wells in the test zone showed high levels of the three by-product gases. For example, on Dec 13, 1996, the control sample showed 73 ppm TCE and none of the other gases, whereas well 2A-03 exhibited a comparable TCE level (78 ppm) but 144 ppb acetylene, 466 ppb ethane, and 223 ppb ethylene. The same is true for intermediate samples as well as for the final samples taken on June 6, 1997. It is thus clear that dechlorination of TCE was definitely occurring in the test zone, but not in the control area.

Table F-2. Water Sampling Results for Various Wells

		Concentration (ppb)					C₂ Ratio
Date	Sample ID	Acetylene	Ethane	Ethylene	cis-DCE	TCE	
	<i>DNAPL TCE Degradation</i>	-	-	-	-	-	>10/0.2/1.0
	<i>Dissolved TCE Degradation</i>	-	-	-	-	-	<0.1/1.0/1.0
3-Dec	<i>Cathode 12/3/96</i>	426	38	168	NA	NA	2.5/0.2/1.0
3-Dec	<i>PZ-2A-02 12/3/96</i>	239	109	140	NA	NA	1.7/0.7/1.0
3-Dec	<i>PZ-2A-03 12/3/96</i>	149	405	177	NA	NA	0.8/2.3/1.0
3-Dec	<i>PZ-2A-04 12/3/96</i>	74	289	198	NA	NA	0.4/1.5/1.0
3-Dec	<i>PZ-2A-05 12/3/96</i>	15	385	113	NA	NA	0.1/3.4/1.0
13-Dec	<i>MW160(control) 12/13/96</i>	ND	ND	ND	ND	73,000	-
13-Dec	<i>PZ-2A-03 12/13/96</i>	144	466	223	ND	78,000	0.6/2.1/1.0
13-Dec	<i>PZ-2A-04 12/13/96</i>	61	262	153	ND	390,000	0.4/1.7/1.0
13-Dec	<i>PZ-2A-05 12/13/96</i>	33	379	165	ND	850,000	0.2/2.3/1.0
10-Jan	<i>PZ-2A-03 1/10/97</i>	143	211	184	NA	NA	0.8/1.1/1.0
10-Jan	<i>PZ-2A-04 1/10/97</i>	94	124	102	ND	200,000	0.9/1.2/1.0
10-Jan	<i>PZ-2A-05 1/10/97</i>	45	127	103	NA	NA	0.4/1.2/1.0
7-Mar	<i>PZ-2A-02 3/7/97</i>	147	ND	108			1.4/0.0/1.0
7-Mar	<i>PZ-2A-03 3/7/97</i>	ND	239	119			0.0/2.0/1.0
7-Mar	<i>PZ-2A-04 3/7/97</i>	57	85	70			0.8/1.2/1.0
7-Mar	<i>PZ-2A-05 3/7/97</i>	75	221	179			0.4/1.2/1.0
7-Mar	<i>Cathode 3/7/97</i>	184	105	221			0.8/0.5/1.0
30-Apr	<i>MW160(control) 4/30/97</i>	ND	ND	ND			-
30-Apr	<i>PZ-2A-03 4/30/97</i>	72	551	252			0.3/2.2/1.0
30-Apr	<i>PZ-2A-04 4/30/97</i>	74	334	92			0.8/3.6/1.0
30-Apr	<i>PZ-2A-05 4/30/97</i>	50	424	268			0.2/1.6/1.0
30-Apr	<i>Cathode 4/30/97</i>	127	ND	62			2.0/0.0/1.0
6-Jun	<i>MW160(control) 6/6/97</i>	ND	ND	ND		61,000	-
6-Jun	<i>PZ-2A-03 6/6/97</i>	59	629	311		45,000	0.2/2.0/1.0
6-Jun	<i>PZ-2A-04 6/6/97</i>	49	306	94		81,000	0.5/3.3/1.0
6-Jun	<i>PZ-2A-05 6/6/97</i>	49	720	297		490,000	0.2/2.4/1.0
6-Jun	<i>Cathode 6/6/97</i>	126	43	89		2,500	1.4/0.5/1.0
9-Jul	<i>MW160(control) 7/9/97</i>	ND	ND	ND		61,000	-
9-Jul	<i>PZ-2A-03 7/9/97</i>	58	816	385		47,000	0.2/2.1/1.0
9-Jul	<i>PZ-2A-04 7/9/97</i>	37	236	66		76,000	0.68/3.6/1.0
9-Jul	<i>PZ-2A-05 7/9/97</i>	91	763	290		280,000	0.3/2.6/1.0
9-Jul	<i>Cathode 7/9/97</i>	183	123	164		2,300	1.1/0.8/1.0

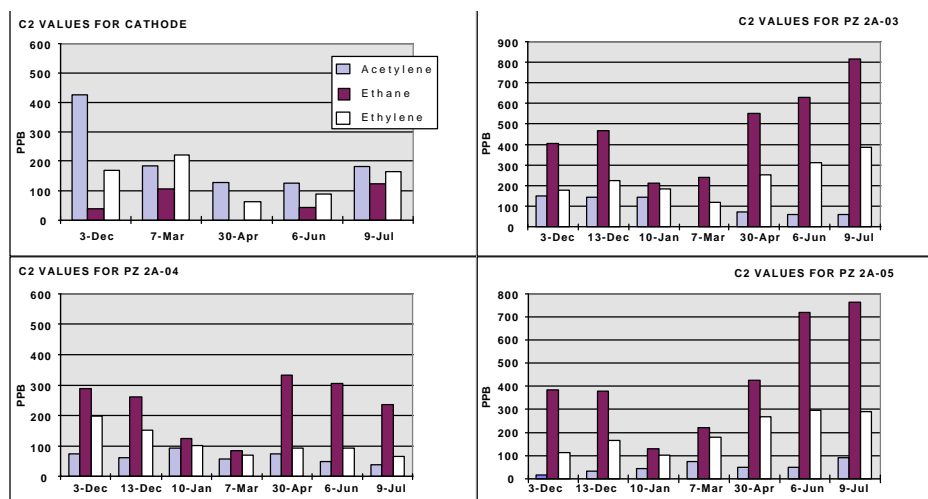


Figure F-9. C2 Degradation Products in Pore Water

Additionally, the pattern of by-product distribution, while varying widely, seemed very consistent with the combination of the two pathways previously discussed for TCE dechlorination. High levels of acetylene, which suggests dechlorination of DNAPL was dominating, accompanied intermediate levels of ethylene and much lower levels of ethane. In contrast, low levels of acetylene, which suggests dechlorination of dissolved TCE was dominating, accompanied much higher levels of ethane and intermediate to comparable levels of ethylene. It should be noted that high levels of the three by-product gases were also detected in the cathode water samples, indicating TCE dechlorination was occurring there as well. This is consistent with results from our laboratory studies.

Carbon Sock Data and Evidence of DNAPL Movement

The four carbon socks inserted in various soil regions (C-01, -02, -04 and -05 in Figure 2) in the test plot were intended to monitor the accumulated movement of TCE in the soil at periodic intervals. After the first 3 months of operation, the first set of carbon socks was recovered and analyzed for TCE and its main daughter products. The results for this first set are shown in Table F-3. Note that TCE distribution is consistent with soil sampling data showing high TCE contamination in the 15- to 25-foot depth regions. One intriguing aspect of these results was the very high levels of TCE found on the carbon. The simple calculation shown at the bottom of Table F-3 illustrates that, even if the soil pore water were 100% saturated with TCE, the amounts of TCE trapped on the carbon for all four socks from the 17- to 23-foot depth were many times higher than all the dissolved TCE in the pore water passing through. These results show clearly that the actual amounts of TCE in the soil were much higher than the average 50 ppm indicated by the pre-test soil sampling. More importantly, some form of DNAPL transport must have occurred to explain the carbon data. This is a significant result, since it suggests that the total treatment time could be significantly shorter than expected, based on TCE transport as dissolved in water. Data at the 4- and 5-month intervals shown in Table F-4 reveal even more accelerated accumulation of TCE on the carbon, probably a consequence of higher soil temperatures. Note that very high levels of TCE were recorded throughout all depths during these periods, suggesting

that vapor transport of TCE was an important factor in the apparent DNAPL movement. It is possible that there could be several mechanisms for enhanced movement of DNAPL TCE in the soil due to increasing temperature: (1), enhanced dissolution rate, (2) EO-induced DNAPL movement due to lower viscosity, and (3) rapid distribution of TCE throughout the soil pore matrix via volatilization/vapor diffusion and re-absorption into the pore water.

Table F-3. First Carbon Sock Sampling Results

Carbon Socks First Sampling, November 13, 1996 Operation Time: 3 months				
Depth (ft)	TCE on Carbon (ppm)			
	C-01	C-02	C-04	C-05
4		83		2
5		52	20	7
6	12	55	18	19
7	17	77	80	36
8	16	22	26	20
9	28	83	26	18
10	23	5,265	52	23
11	69	9,306	33	27
12	2,064	6,562	11	65
13	6,937	5,595	11	161
14	9,465	8,199	80	369
15	14,714	24,392	115	816
16	29,704	41,436	100	2,715
17	81,420	105,190	1,747	3,441
18	116,989	136,687	54,230	9,029
19	118,259	154,094	31,377	24,221
20	126,433	169,319	53,571	18,591
21	102,790	150,946	41,457	70,617
22	116,964	81,176	17,900	94,812
23	130,106	103,850	140,714	139,821
Total TCE (g)	123	144	49	53
Calculations:				
Carbon sock is 1.5 inches diameter, contains 144 grams wet carbon/ft.				
Sock sectional area per foot in direction of flow = 116 cm ² .				
At EO flow velocity of 0.8 cm/day, amount of water flowing into sock is equal to: 116 cm ² x 0.8 cm/day x 0.4 (porosity) = 37.1				
If water is saturated with TCE (1,100 mg/l), amount of TCE absorbed per foot of carbon sock for 3 months is:				
1100 mg/l x 37.1 cm ³ /day x 0.001 l/cm ³ x 90 days = 3.67 g TCE.				
Average TCE loading on carbon for the 3 months time under saturated conditions = 3.67 g TCE / 144 g carbon = 25,500				
TCE loadings on C-01 and C-02 from 17 to 23 ft are thus many times the saturation level, which suggests DNAPLs movement.				

Table F-4. Carbon Sock Sampling Data for Second and Third Events

TCE on Carbon (ppm)					
Second Sampling, Dec 13, 1996 Operation Time : 4 months Carbon Sock Time : 1 month			Third Sampling, Jan 09, 1997 Operation Time : 5 months Carbon Sock Time		
			2 months		1 month
Depth (ft)	C-02	C-05	C-01	C-04	C-05
1	405,541			1,632	124,667
2	394,541		61,675	481	87,697
3	411,029	69	46,871	268	86,942
4	429,261	43	32,936	272	34,281
5	389,354	56	22,815	846	15,828
6	403,701	32	19,093	7,491	Bentonite
7	303,303	59	15,708	12,821	809
8	296,435	98	11,941	1,560	569
9	212,292	126	10,568	7,111	1,205
10	242,627	176	12,053	6,948	3,915
11	257,343	86	15,316	7,134	4,522
12	140,342	285	20,949	4,829	Bentonite
13	259,092	440	31,085	8,346	Bentonite
14	293,527	436	64,185	6,469	3,500
15	262,147	226	100,286	17,723	1,251
16	266,120	686	149,777	10,573	3,950
17	225,826	878	164,884	22,929	10,707
18	269,942	1,235	183,357	32,704	13,815
19	262,363	1,522	237,793	50,202	40,957
20	262,561	4,099	207,050	49,155	128,510
21	261,774	11,487	241,157	72,523	18,521
22	227,243	17,844		58,740	71,479
23	252,027	51,789		30,422	
24	286,678	61,624		55,553	
				53,131	
Total TCE (g)	631	14	148	47	39

With the carbon samples and piezometers indicating very high levels of TCE, a large amount of DNAPL was probably present in the southern portion of the experiment plot. The initial soil sampling did confirm the presence of DNAPL but not at the levels indicated by the carbon samples. The carbon sock data are graphically summarized in Figure F-10 and shown in more detail in Appendix C.

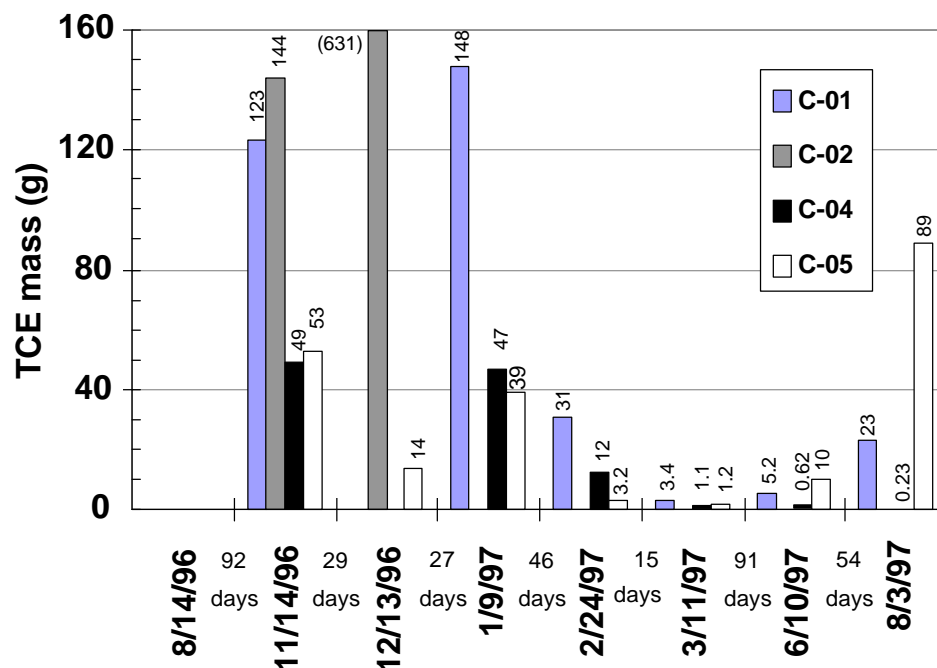


Figure F-10. TCE Amounts in Carbon Sock Monitors

Soil Data and TCE Removal Estimates

While the water data and dechlorination results were interesting, the decisive factor in determining whether the *Lasagna*TM process was successful in cleaning up the plot rested upon actual soil samples. The site operators and the State of Kentucky had negotiated a clean up target of 5.7 mg of TCE per kg of soil (ppm). This level was based on assessment modeling of the groundwater reaching the fence line. *Lasagna*TM would be considered successful if the average of the soil samples was less than 5.7 mg/kg. The soil sampling procedure called for at least 5 sample locations and soil samples taken at 1-foot intervals in the bore holes from 5 to 40 feet deep, as described in the experimental section.

The soil sampling results of the three soil sampling events - pre-test, mid-test, and post-test - are summarized in Table F-5. The pre-test soil sampling was performed in March, 1996. The data in Table F-5 show that the TCE concentrations in the soil ranged from non-detected to approximately 360 mg/kg (ppm) for any single soil sample. Sample point 2A-03 had the highest average TCE concentration (50 mg/kg), followed by 2A-02, 2A-05, 2A-04 and 2A-01. This soil sampling event shows there was DNAPL in the area of 2A-03, 2A-04 and 2A-05. More detailed soil data are included in Appendix D.

Table F-5. Soil Sampling Results

Sample Point		Mar-96	Mar-97	Aug-97	Removal	Number of Pore Volumes
2A-01	Min	nd		nd		
	Max	125		10.6		
	Avg	18.4		0.886	95.2%	1
2A-02	Min	.106	nd	nd		
	Max	148	1503	106		
	Avg	42.1	89.6	23.9	43.2%	<1
2A-03	Min	nd	nd	nd		
	Max	309	27.4	1.48		
	Avg	50.8	2.20	0.150	99.7%	2+
2A-04	Min	nd	nd	nd		
	Max	152	65.8	47.9		
	Avg	33.6	12.9	9.46	71.8%	<1
2A-05	Min	.188	.050	nd		
	Max	123	116	64.4		
	Avg	31.4	16.4	9.19	70.7%	<1

Results of the mid-test soil sampling conducted in early March, 1997, after 6 months of operation, were encouraging. The sampling was modified slightly to include samples at all soil strata interfaces as well as the 1-foot intervals. The purpose of this intermediate sampling event was to determine whether the LasagnaTM process was effective and whether DNAPL was still present. The soil samples near 2A-03, which was located between the 2-foot spaced treatment zones, indicated 95% removal of TCE. Since 2A-03 had the highest average pre-test TCE levels, the process was clearly effective, even with the presence of DNAPL. Soil samples near 2A-04 showed a 60% cleanup while the 2A-05 samples showed 50% cleanup. It is possible that some reverse movement of TCE in areas of high concentrations may have slowed the apparent clean-up of areas 2A-04 and 2A-05. The soil samples near 2A-02, which is an upstream location, showed very high amounts of TCE.

The post-test samples taken in August, 1997, show a continued decline in the soil TCE concentrations. Most impressively, sample 2A-03 dropped to an average of less than 0.2 ppm with the highest single sample measuring 1.5 ppm. Sample points 2A-04 and 2A-05 had average TCE concentrations above the 5.7 ppm target but showed steady progress with approximately 70% removal. Sample point 2A-01 showed excellent clean up with 95% removal and an average soil TCE concentration of less than 1 ppm. The upgradient sample point, 2A-02 has cleaned up slightly, but the results over the three sampling events are erratic. While the results from sample point 2A-02 are inclusive, its upgradient location suggests it is unlikely that any significant TCE removal has occurred, because the "clean front" of pore water would not yet have reached this location according to flow rate

measurements and electro-osmotic permeability calculations. The soil sample results for the five locations are presented in Figures F-11 - F-15.

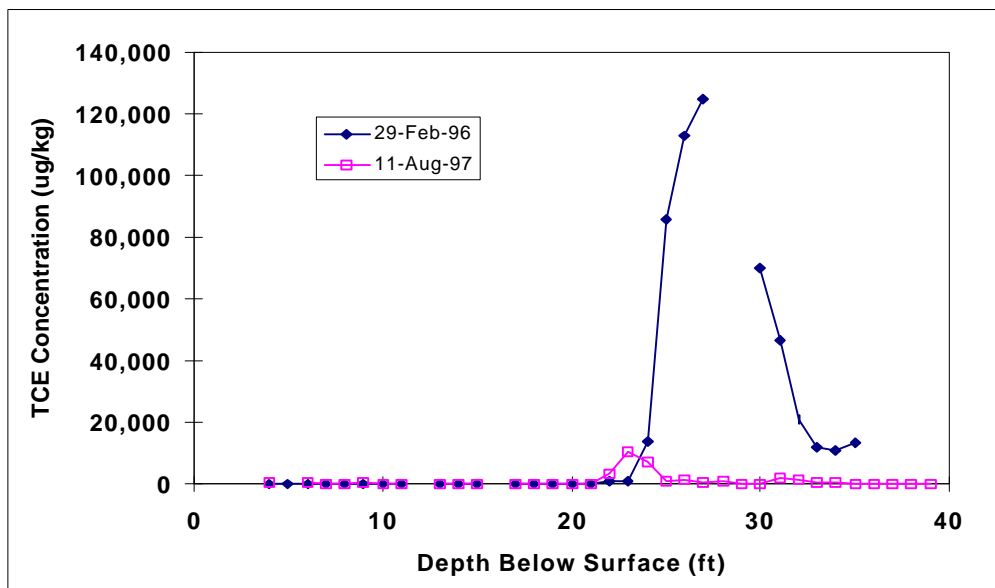


Figure F-11. Soil TCE Concentrations for Sample Point 2A-01

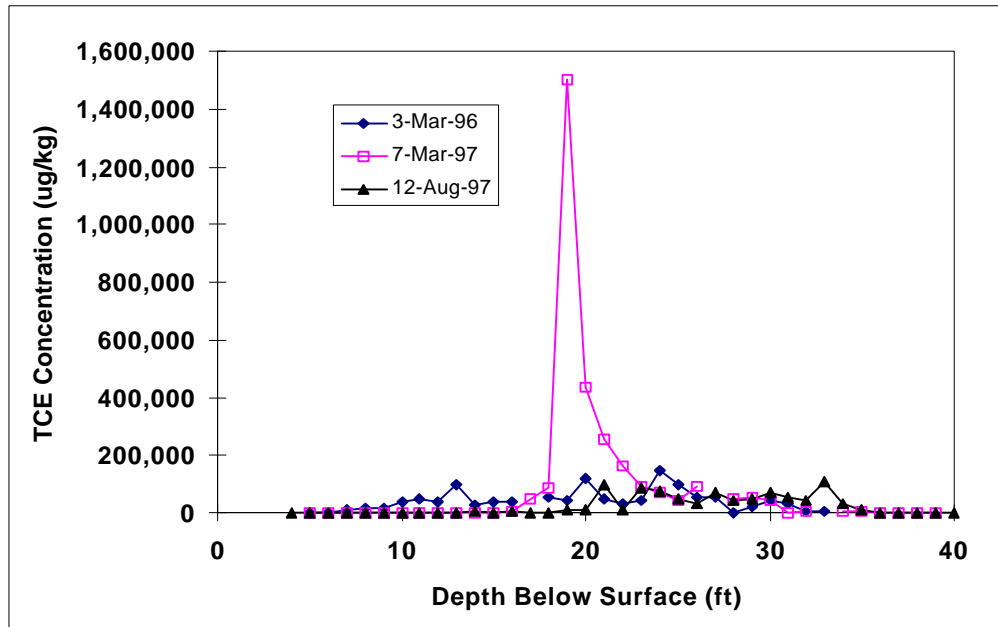


Figure F-12. Soil TCE Concentrations for Sample Point 2A-02

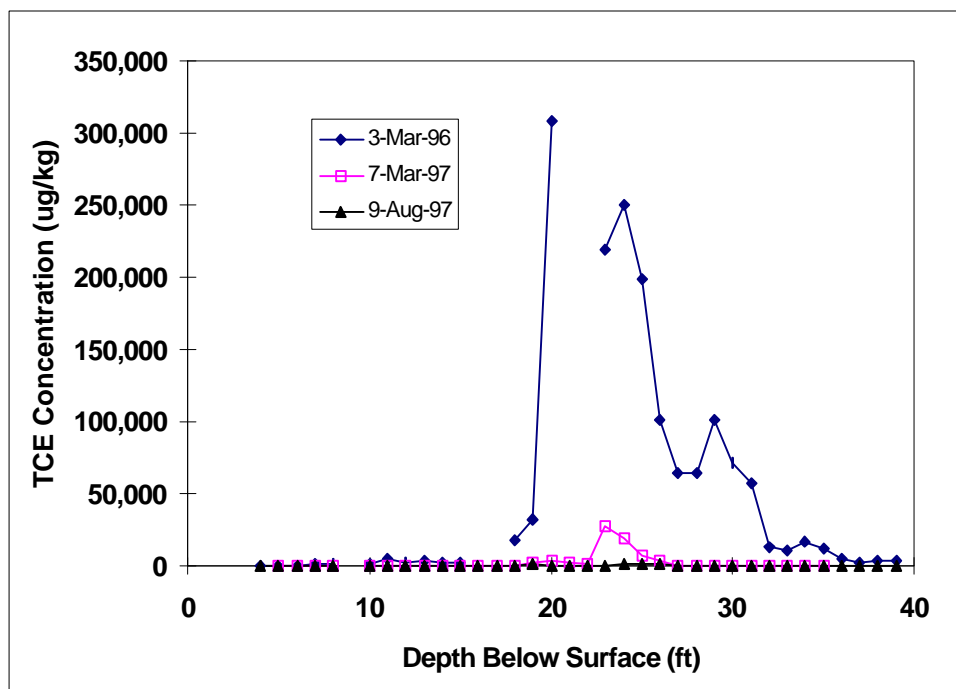


Figure F-13. Soil TCE Concentrations for Sample Point 2A-03

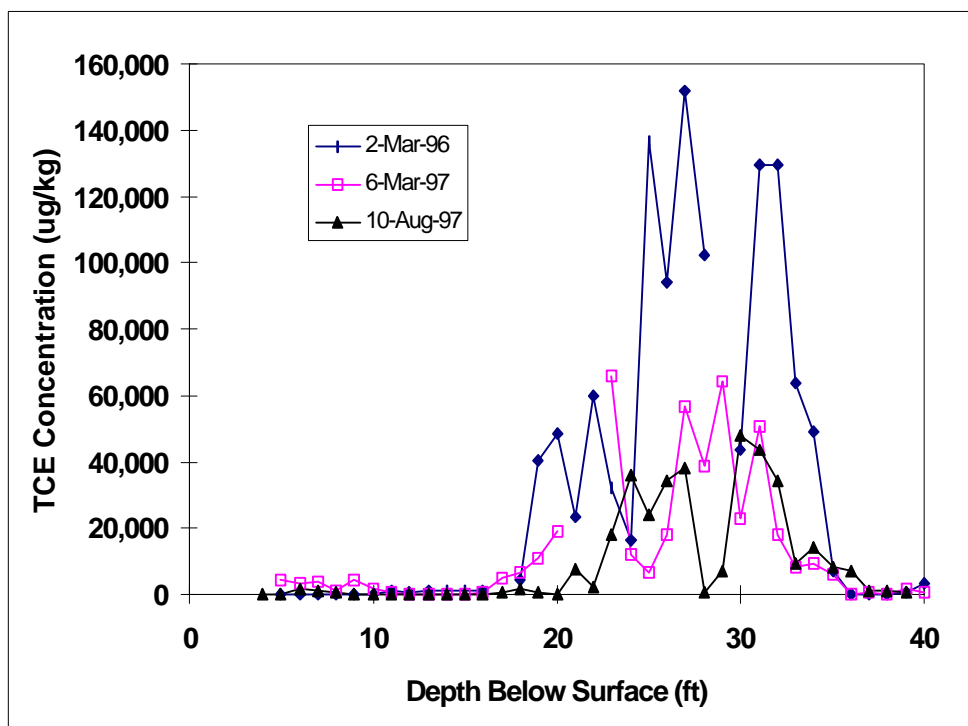


Figure F-14. Soil TCE Concentrations for Sample Point 2A-04

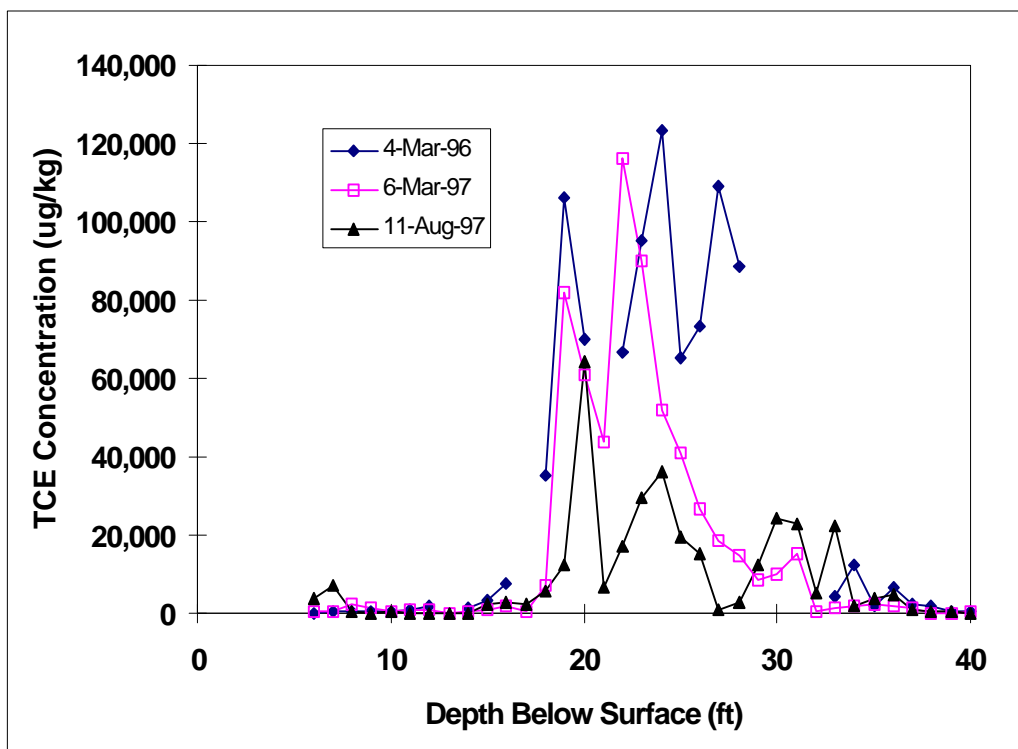


Figure F-15. Soil TCE Concentrations for Sample Point 2A-05

Volatilization Testing

Since the soil was heated to an average temperature of 60°C (>80°C at the center core) by the end of the field test, there was concern that an unknown percentage of the TCE was possibly being volatilized into the surrounding atmosphere instead of being dechlorinated by electro-osmosis, thus causing a health hazard and leading to an erroneous conclusion on the effectiveness of the technology for TCE cleanup. To address this concern, emissions were monitored twice during the test using an EPA-certified flux chamber method, the first time about half way into the test and the second near the end when the soil temperature was the highest. The flux chamber method is the most commonly used air sampling procedure to determine gaseous emissions from landfills and impoundments. No significant TCE emissions, including its daughter products, were detected. The cold surfaces of the 4-foot gravel layer and a layer of treatment zone materials spread above the gravel may have resulted in condensation of any TCE emissions and thus helped contain them. The flux chamber data is presented in Appendix E.

Conclusions

Based upon these results, it is concluded that the *Lasagna*TM technology has demonstrated the capability to effectively dechlorinate TCE contamination in situ, including DNAPL concentrations, in low-permeable soil to a depth of 45 feet. An existing emplacement method with a hollow mandrel was effectively adapted for installing electrodes and treatment zones in thin layers through stiff clay soil without generating solid waste. The electrokinetic aspects of the field demonstration, such as water flow rate, voltage, and current distribution, power consumption, and extent of temperature rise and temperature profile in the soil correlate well with the pilot and laboratory experiments. These results were also in good agreement with a mathematical model developed from Phase I. Inexpensive, innocuous, and easily handled materials such as granular coke and iron filings were found to be effective for forming electrodes and treatment zones. This was the first time that iron filings mixed with clay to form a slurry has been shown to be effective for degrading TCE in an electrokinetic environment. There are strong indications that some of the TCE could have been transported and degraded in the DNAPL form. Soil samples taken at several key locations and down to the 45-foot depth indicated that two pore volumes of electro-osmotic flow between the adjacent treatment zones were sufficient to reduce TCE contamination levels to below the cleanup target of 5.7 ppm, even in regions containing DNAPL. The overall removal efficiency obtained was in the range of 95% for 1 pore volume to over 99% for 2.6 pore volumes. Implemented for the first time under actual field conditions and with the unexpected complications of much higher than expected DNAPL levels and complex hydrogeology in the subsurface, the *Lasagna*TM process has demonstrated its robustness and flexibility in cleaning up TCE-contaminated soil *in situ*.

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Appendix A. Field Data Electrokinetic Data Spreadsheets

Appendix B. Water Sampling Analysis and Summary Spreadsheets

Appendix C. Carbon Sock Data Spreadsheets

Appendix D. Summary of Soil Sampling Data

Appendix E. Summary of Flux Chamber Results
